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LONG RANGE BASIC RESEARCH LEADING TO THE DEVELOPMENT OF
SUPERIOR PROPELLANTS.

Compounds of High Nitrogen Content in
Propellent Compositions

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Project No. TAL-5006B, Item P

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Prepared by:

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Agency Authorizing Work: Ordnance Research & Development Division, ORDTA

Project No.: TAL-5006B, Item P

DOA Priority Designation: 2A

Project Title: Long Range Basic Research Leading to the Development of Superior Propellants - Compounds of High Nitrogen Content in Propellant Compositions.

OBJECT

To synthesize and evaluate new high nitrogen compounds of possible interest for use as flash and smoke reducing agents in propellant powders.

SUMMARY

Twelve high nitrogen compounds have been investigated in the laboratory as possible ingredients for propellant compositions for purposes of improving performance. Of these compounds, carbonylhydrazide oxalate, dinitrobiuret, diaminobiuret, hydrazine oxalate and hydrazine nitrate were found to be either unstable by themselves or not compatible with nitrocellulose and therefore of little value militarily.

Urazine, N-guanyloxamic acid and cyamelide are inert, stable compounds of low energy content and good physical properties. Although these materials may yield satisfactory cool compositions, their present method of preparation does not make them feasible for large scale production.

Although nitrobiuret undergoes decomposition at 100°C, it appears sufficiently stable and compatible with nitrocellulose at 75°C. This compound is of particular interest as a non-smoky flash reductant because it possesses a zero oxygen balance to carbon monoxide and water, requires energy to burn, and can be made readily available.

Guanylamino-tetrazole and guanylamino-tetrazole nitrate, which contain 77% and 56% nitrogen, respectively, both possess negative energy contents for combustion but because of their phosphoric nature can be made to burn readily. Both compounds possess good physical properties and are compatible with nitrocellulose. Calculations indicate that they should yield cool compositions with good ballistic potential.

Using extreme nitration conditions, very small yields of nitroguanylamino-tetrazole (65%N) have been obtained from guanylamino-tetrazole. This

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nitramine has never been previously described in the literature. A partial evaluation of this material indicates that it may have excellent potentialities as an ingredient for low temperature, high "force" propellants. A theoretical discussion based on the internal ionic character of 5-aminotetrazoles, is presented to explain the reluctance of guanylamino-tetrazole to nitrate to the corresponding nitramine. An alternative indirect method of synthesis for this compound is proposed.

CONCLUSIONS

Carbohydrazide oxalate, dinitrobiuret, diaminobiuret, hydrazine oxalate and hydrazine nitrate are not suitable as addends to nitrocellulose propellants because of poor stability characteristics. Urazine, N-guanyloxamic acid and cyamelide have satisfactory properties as inert, non-smoky flash reductants but, as they are difficult and costly to manufacture, are not now worthy of consideration beyond the laboratory stage.

Nitrobiuret may prove to be sufficiently stable and compatible in nitrocellulose compositions to provide an economical cool propellant ingredient.

Both guanylamino-tetrazole and its nitric acid salt are worthy of further consideration and investigation as cool, high potential propellant ingredients.

RECOMMENDATIONS

It is recommended that experimental compositions containing nitrobiuret, guanylamino-tetrazole and guanylamino-tetrazole nitrate be prepared and subjected to laboratory and ballistic tests to further determine the suitability of these compounds.

It is also recommended that an indirect synthesis for nitroguanylamino-tetrazole be investigated in the laboratory, namely, using biguanide as a starting material.

It is suggested that future research on new high nitrogen compounds be continued with a major emphasis on tetrazole derivatives as these materials appear to offer promise as coolants in high potential propellants.

Since high nitrogen compounds of possible use for ordnance materials can be derived from hydrazine, it is recommended that a program be initiated to investigate economical methods for the production of this basic ingredient.

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INTRODUCTION:

1. The successful incorporation of nitroguanidine in compositions to produce a "cool", flashless propellant has resulted in an increased study of all types of high nitrogen compounds as possible non-smoky flash reductants. Compounds of high nitrogen content are desirable as propellant ingredients because they generally yield non-combustible muzzle gases of a greater volume and lower temperature than those produced by the more standard propellant ingredients. Research at Picatinny Arsenal has been directed towards investigating derivatives of guanidine, urea and hydrazine and evaluating these derivatives as to their suitability in improving propellant performance.

2. This report summarizes the chemistry and properties of twelve high nitrogen compounds not previously considered as propellant ingredients. In addition, using the system nitrocellulose-explosive plasticizer-high nitrogen compound-stabilizer, calculations on hypothetical compositions containing the more suitable of the twelve compounds are presented and compared with the standard nitroguanidine Propellant (M-15).

RESULTS:

3. Laboratory test data for the twelve compounds studied are recorded in Tables I, II, III and IV. These results are summarized as follows:

a. Urazine and N-guanyloxamic acid are inert, non-hygroscopic and thermally stable compounds. Both are compatible with nitrocellulose at 100°C. Urazine is moderately soluble in water whereas N-guanyloxamic acid is practically insoluble.

b. Carbohydrazide oxalate is an inert, non-hygroscopic, slightly water soluble salt. It decomposes slowly at 100°C but is fairly compatible with nitrocellulose at that temperature.

c. Nitrobiuret is non-hygroscopic, slightly soluble in water and organic solvents and slightly sensitive to impact. It gives an acid reaction with water but a saturated aqueous solution, on standing, hydrolyzes slowly to the basic side. It is unstable at 100°C but stable and compatible with nitrocellulose at 75°C.

d. Dinitrobiuret and diaminobiuret are both thermally unstable and incompatible with nitrocellulose. The former compound is quite sensitive to impact.

e. Cyamelide is a very inert, very insoluble, white, polymeric material. The sample prepared in the laboratory was found to be 5% hygroscopic at 90% RH, thermally stable, and quite compatible with nitrocellulose.

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RESULTS: (contd)

f. Hydrazonium oxalate is inert, moderately soluble in water and non-hygroscopic. Although fairly stable by itself at 100°C, it is incompatible with nitrocellulose at that temperature; at 75°C, however, it is more compatible.

g. Hydrazonium nitrate is very soluble in water and deliquescent at 90% RH. Although it melts at 71°C, it is extremely stable at 100°C; however, it is incompatible with nitrocellulose at 75°C and exhibits explosive properties.

h. Guanylaminotetrazole is a non-hygroscopic, practically insoluble compound containing 77% nitrogen. The material was found to be inert, thermally stable, and compatible with nitrocellulose.

i. Guanylaminotetrazole nitrate is moderately soluble in water, sensitive to impact and explodes at 180°C. This salt, which crystallizes with half a molecule of water, loses its water very slowly at 100°C. The resulting anhydrous form is stable at that temperature. The hemi-hydrate, which is non-hygroscopic, is compatible with nitrocellulose at 100°C.

j. Nitroguanylaminotetrazole is extremely insoluble in water and the common organic solvents, stable at 100°C, and thermally compatible with nitrocellulose.

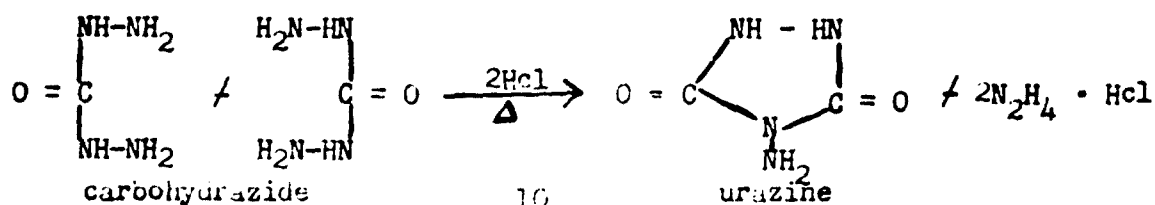
4. The infrared absorption spectra of cyanamide and cyanuric acid, recorded from solid phase mulls, are presented in Figure 1.

5. The thermochemical properties related to ballistic performance have been calculated from the observed heats of combustion of the above compounds and are listed in Table VI. Nitroguanidine is included as a basis for comparison.

6. Calculations of internal ballistic properties have been made on hypothetical compositions containing the most suitable of the high nitrogen compounds and are recorded in Table VII.

DISCUSSION OF RESULTS:

7. When carbohydrazide is heated in the presence of acid catalysts, a condensation reaction occurs accompanied by a cyclization to form urazine (Ref A). This reaction is best represented as:

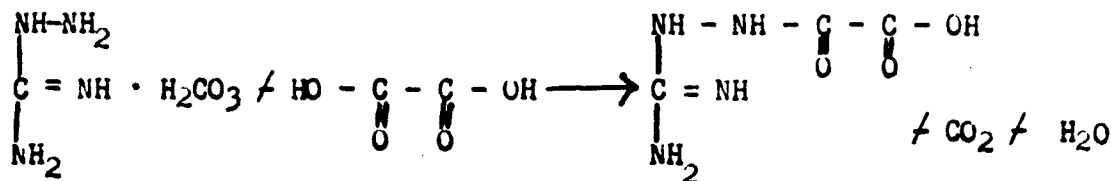


DISCUSSION OF RESULTS: (contd)

Carbohydrazide, itself, is mildly basic, highly soluble in water and relatively unstable. Urazine, however, is only moderately soluble in water with a slight acid reaction and is very stable to heat. It is compatible with nitrocellulose and possesses properties indicative of a good propellant ingredient. Compositions with nitrocellulose can be formulated, containing about 20% urazine, which have lower flame temperatures and better oxygen balance than M-15 Propellant. However, the best urazine composition with $T_v < 2600^\circ K$ will give 8% less ballistic potential or "force" than the nitroguanidine powder.

8. When aqueous solutions of carbohydrazide and oxalic acid are mixed, a relatively insoluble, non-hygroscopic salt precipitates, consisting of equimolar amounts of acid and base (Ref A). The thermochemical properties of this salt indicated that it would be a good "coolant" and yet not too "smoky". However, the stability of carbohydrazide oxalate at elevated temperatures is questionable. Since it does not compare as favorably in overall properties as some of the other compounds studied, its further consideration as a propellant ingredient is not recommended.

9. When aminoguanidine bicarbonate and oxalic acid are allowed to react in hot aqueous solution, evolution of carbon dioxide takes place and a fine, dense, white precipitate of N-guanyloxamic acid forms (Ref A).



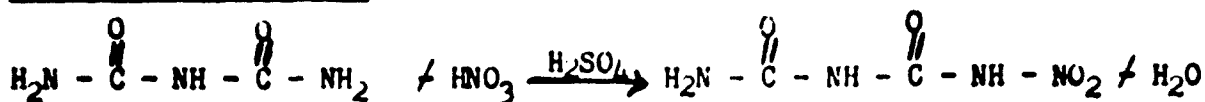
N-guanyloxamic acid is highly insoluble in water and organic solvents, quite stable at elevated temperatures and compatible with nitrocellulose. Calculations indicate that it can be incorporated in 15% by weight with nitrocellulose to give a cooler, better oxygen-balanced propellant than M-15 but with 10% less ballistic potential.

10. Biuret can be considered as a condensation product of urea, derived as the result of the loss of a molecule of ammonia from two of urea. It is obtained by heating urea for a long period of time at $160^\circ C$ (Ref B). Since biuret has low solubility in water and is fairly stable at higher temperatures, it was believed that its nitrated and other high nitrogen derivatives might be more stable and have better physical properties than the analogous urea derivatives.

11. Nitrobiuret can be obtained readily upon treatment of anhydrous biuret with mixed acid (Ref C).

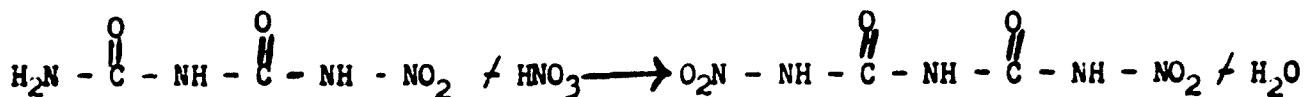
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DISCUSSION OF RESULTS: (contd)



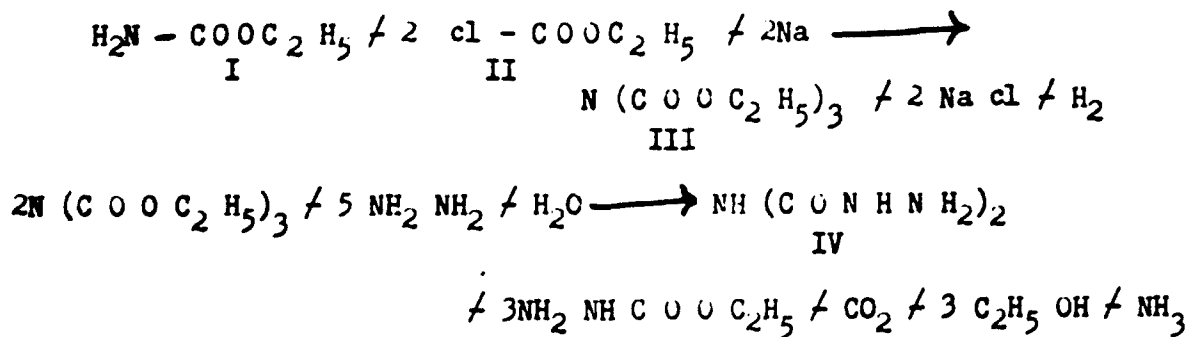
Nitrobiuret is non-hygroscopic, only moderately soluble in water, and a saturated aqueous solution at 60°C hydrolyzes slowly from a pH of 1.8 towards the basic side. It is not stable at 100°C but does not decompose appreciably at 75°C and at that temperature appears compatible with nitrocellulose. Although its oxygen balance to carbon monoxide and water is zero it still requires more energy than nitroguanidine for complete combustion and, therefore, from a thermochemical viewpoint, should make an excellent "coolant" ingredient for propellant compositions.

12. Nitrobiuret can be nitrated further, under extreme conditions, to form dinitrobiuret. Based on a method of Thiele and Uhlfelder (Ref C), this compound was prepared by dissolving nitrobiuret in excess 100% nitric acid and then concentrating in the dark from a vacuum dessicator containing concentrated sulfuric acid and soda lime (separated from each other).



Dinitrobiuret, which possesses an oxygen balance of $\neq 21\%$ to CO and H₂O, decomposes slowly in water with an acid reaction. It is quite sensitive to impact and explodes at 165°C. Since it decomposes completely at 75°C, no further consideration will be given to this material as a propellant ingredient.

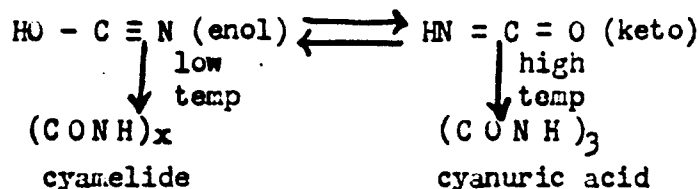
13. It was decided to study the properties of diaminobiuret because this material contained 53% nitrogen, possessed a large gas volume (0.060 mole /gm) and offered good "coolant" characteristics. However, the compound can not be prepared from biuret directly. The best method of preparation of diaminobiuret (Ref D) involves a two-step synthesis starting with a condensation between urethane (I) and ethylchlorocarbonate (II) to give nitrogen tricarboxylic acid ethyl ester (III). The ester (III) is then allowed to react with hydrazine to yield both diaminobiuret (IV) and ethyl hydrazine carboxylate (V). This series of reactions can be represented as:



DISCUSSION OF RESULTS: (contd)

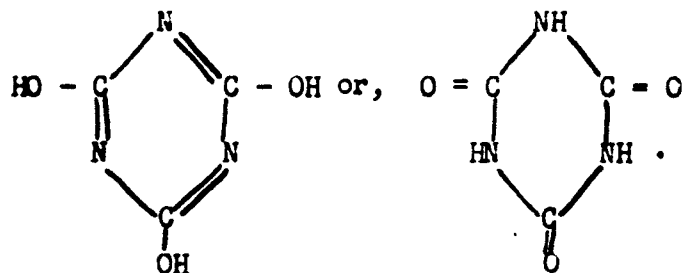
Diaminobiuret is a white, non-hygroscopic material melting at 200°C with decomposition. It was found to be very soluble in cold water, not too stable at 100°C and incompatible with nitrocellulose. As a result of these poor characteristics this material is not suitable as a propellant ingredient.

14. In an effort to find "cool burning" nitrogen compounds that are not too poorly oxygen-balanced, it was decided to investigate the two solid polymeric forms of cyanic acid, namely, cyanuric acid and cyamelide. Free cyanic acid itself is a colorless, unstable, volatile liquid which is strongly acidic and raises painful blisters on the skin. At 0°C it is stable for short periods, gradually polymerizing to form mixtures of cyanuric acid and cyamelide. Werner and Fearon (Ref E) suggested that cyanic acid exists in two tautomeric forms, the enol form which is stable only at low temperatures and the more stable keto form. The enol form polymerizes to a white amorphous material, cyamelide, whose structure has not yet been established with certainty. At higher temperatures and also in the gas phase, the keto form gives rise to a trimer, cyanuric acid, whose structure is known to contain the tricyanogen ring. These transformations can be represented as follows:



At 0°C, Werner and Fearon found that free cyanic acid polymerizes into a mixture containing 60% cyamelide and 40% cyanuric acid indicating the respective amounts of enol and keto form present at that temperature. At higher polymerization temperatures, they found that the percentage of cyanuric acid increased and that of cyamelide decreased.

15. Cyanuric acid behaves as a monobasic acid when titrated with dilute alkali using phenolphthalein as indicator. This fact along with the many different derivatives that it forms (Ref F), gives concrete evidence that it contains the symmetrical triazine ring. Its structure may be represented as:



DISCUSSION OF RESULTS: (contd)

This material, which is slightly soluble in water, crystallizes out as a dihydrate which is efflorescent in air. The anhydrous form recovers all of its water (22%) at 90% RH and 30°C. For this reason alone, no further consideration was given to cyanuric acid as a propellant ingredient.

16. As stated in paragraph 14, cyamelide can be prepared along with cyanuric acid by polymerizing cyanic acid at 0°C. Cyanic acid in turn is prepared by the depolymerization of cyanuric acid with heat or by the action of anhydrous acids on metal cyanates. Using a method described by Hantzsch (Ref G), small yields of cyamelide were obtained by grinding together potassium cyanate and crystalline oxalic acid. A sample prepared in this manner gave an elemental analysis (Table I) indicative of an empirical formula $(\text{CUNH})_x$ and yielded no titration with dilute sodium hydroxide (as distinguished from cyanuric acid). According to Sidgwick (Ref F) "cyamelide forms no salts with the alkalis under any conditions and hence it is very unlikely to contain hydroxyl groups or the amide grouping, $\text{H N} - \text{C} = \text{O}$. It does, however, form a mercury derivative and hence may well contain imide groups, $\text{>C} = \text{NH}$. If boiled with water it gives ammonia and carbon dioxide together with some cyanuric acid, and prolonged treatment with alkalis converts it into the alkali salt of cyanuric acid." On the basis of these properties, Sidgwick suggests that cyamelide is a linear polymer of high molecular weight with a structure

$$- \text{O} - \overset{\text{NH}}{\underset{\text{||}}{\text{C}}} - \text{O} - \overset{\text{NH}}{\underset{\text{||}}{\text{C}}} - \text{O} - \overset{\text{NH}}{\underset{\text{||}}{\text{C}}} - \text{O} \dots$$

17. The sample of cyamelide prepared at Picatinny was found to be highly insoluble in water and the usual organic solvents. It is inert, does not melt at 300°C, and is 5% hygroscopic at 90% RH and 30°C. The material is stable at 100°C and compatible with nitrocellulose. A saturated aqueous solution at 60°C hydrolyzes very slowly towards the acid side. Cyamelide requires a great deal of energy to burn but possesses an oxygen balance to carbon monoxide and water of only -19%. As a result, it is of interest to propellant formulation strictly as a non-smoky "coolant", since it is possible to formulate compositions that yield flame temperatures of 2500°K or less containing only 10% cyamelide.

18. It was decided to compare the infrared spectra of cyanuric acid and cyamelide with the hope that some definite knowledge would be gained concerning the structure of the latter compound. Since no suitable organic solvent was known for either compound, the spectra were recorded from solid phase mills of the two substances (Figure 1). Despite the poor resolution obtained, the spectrum of each compound definitely indicates a different molecular configuration. However, no inference as to functional groupings can be drawn at present, due to insufficient spectral data of related known compounds.

DISCUSSION OF RESULTS: (contd)

19. A review of the literature (Ref H) indicated that most of the mono-acid salts of hydrazine were fairly stable and did not hydrolyze in aqueous solution. It was decided to investigate the properties of hydrazine oxalate (or hydrazonium hydrogen oxalate) because calculations showed that it would behave as an effective "coolant" while possessing a high molar gas volume (0.0492 mole /gm) and an oxygen balance to CO and H₂O of -13%. The salt is prepared easily by mixing concentrated solutions of hydrazine hydrate and oxalic acid. It crystallizes out of a hot aqueous solution in fine, non-hygroscopic needles and when heated begins to decompose at 181°C. It is moderately soluble in cold water, reacts acid in aqueous solution but does not hydrolyze on standing. This salt, although stable by itself at 100°C is not compatible with nitrocellulose at that temperature. At 75°C, its compatibility with nitrocellulose is also questionable. As a result, hydrazine oxalate is not recommended for use as an addend to nitrocellulose propellants.

20. It was reported (Ref H) that the mono nitric acid salt of hydrazine, which melts at 71°C, shows no sign of decomposition even at 300°C. Although hydrazine nitrate was also listed as being very soluble in water and hygroscopic, it was decided to investigate this material because it possesses, in its constitution, all the inherent characteristics of a monopropellant, containing both a fuel and an oxidant in its molecule. Hydrazine nitrate is also of interest as a solid propellant because it contains no carbon and possesses 8% excess oxygen required for combustion to N₂ and H₂O. A sample of the salt was prepared by carefully mixing equivalents of hydrazine hydrate and nitric acid in concentrated solutions. The product lost no weight when heated at 100°C for 96 hours and evolved only 0.02 ml gas per 5-gm sample in 40 hours when subjected to the 120°C Vacuum Stability Test. It was found to be very soluble in cold water, insoluble in anhydrous organic solvents and deliquescent at 30°C and 90% RH. The material behaves as an explosive being sensitive to impact (13" 2 kgm wt, PA Machine) and is almost as brisant as Tetryl. When ignited in the open, it burns rapidly with no visible gaseous products. It is not sensitive to friction. When a film of hydrazine nitrate and nitrocellulose was prepared, containing 25% of the salt, the nitrate appeared to become plasticized along with the nitrocellulose. Evidently, the salt dissolved completely in the solvent (ethyl methyl ketone) due to the presence of a slight amount of moisture. However, this film lost about 20% of its weight at 75°C in 96 hours. It is interesting to note that, although hydrazine nitrate melts at 71°C, the film did not appear to change its physical form appreciably when heated above that temperature, thus indicating that the salt forms a true colloid with nitrocellulose. Because of its poor compatibility, hydrazine nitrate can not be considered as an ingredient for nitrocellulose propellants. However, if a suitable polymeric or resinous material can be found, which

DISCUSSION OF RESULTS: (contd)

when combined with hydrazine nitrate reduces its hygroscopicity, the salt may be of interest as a castable solid rocket fuel ingredient.

21. The study of tetrazole derivatives has always occupied a major portion of the investigation of high nitrogen compounds at Picatinny Arsenal. These compounds appear to offer the greatest advantage as non-smoky flash reductants, especially where the highest percentage of nitrogen is desirable. Tetrazole itself is a fairly acidic, relatively unstable compound and may exist in the tautomeric forms I and II, the position of a hydrogen atom occupying either the 1 or 2 position:



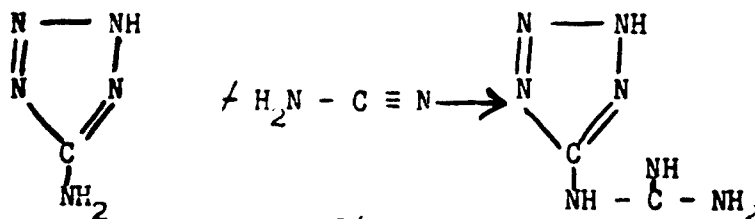
I



II

Both hydrogen atoms in the tetrazole molecule are labile and literally hundreds of mono and disubstituted derivatives have been prepared (Ref I). The tetrazole ring can also be considered as a phosphore, the compound being explosive when heated and also sensitive to impact. Many of the substituted tetrazoles, however, are considerably less explosive and more thermally stable than the parent nucleus. One of the most studied of such derivatives is 5-aminotetrazole, which is of particular interest to the propellant field as a "coolant" because the compound contains 83% nitrogen, possesses a large gas volume, requires energy to burn and yet can be incorporated in propellant compositions, in fairly large proportions, without appreciably slowing down the burning rate (Ref J). Unfortunately, however, 5-aminotetrazole crystallizes with one molecule of water which is readily lost at slightly elevated temperatures while the resulting anhydrous form is very hygroscopic. Since this molecule of water represents 21% by weight of the entire compound, 5-aminotetrazole can not be readily used as a propellant ingredient unless this affinity for water can be reduced.

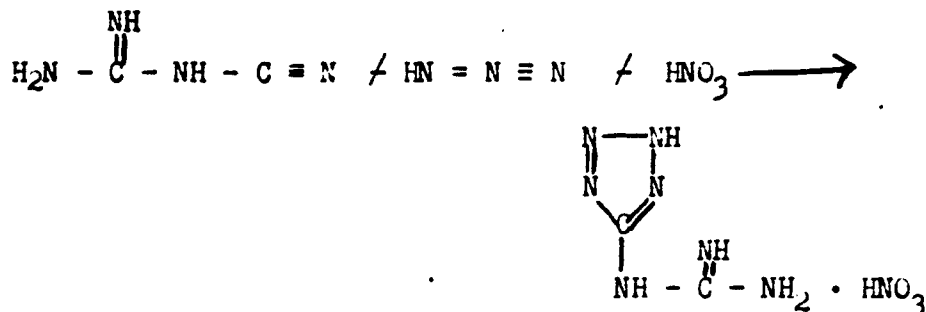
22. R. Stollé, in his investigation of tetrazole derivatives, was able to condense cyanamide with 5-aminotetrazole to yield 5-guanylamino-5-aminotetrazole (Ref K).



DISCUSSION OF RESULTS: (contd)

As this compound possesses 77% nitrogen and was reported as being stable up to 300°C, it was decided to investigate it as a possible propellant ingredient. Since free cyanamide is not available commercially, both aqueous and alcoholic solutions of the material were prepared in the laboratory from crude commercial calcium cyanamide (See paragraph 39). Upon addition of 5-aminotetrazole to either of the above solutions and heating the resulting mixture on a steam bath for four or more hours, yields of 50% or better of guanylamintetrazole (based on 5-aminotetrazole) were obtained. The pure material, obtained after recrystallization from hot water, did not melt when heated to 300°C. It was non-hygroscopic and only slightly soluble in cold water. Guanylamintetrazole reacts slightly acid with water but a saturated aqueous solution does not hydrolyze significantly after standing at 60°C for 24 hours. The compound possessed good stability when subjected to both the 100°C Heat and 120°C Vacuum Stability Tests and was thermally compatible with nitrocellulose. It could not be detonated at 40 inches using a 2-kgm weight. Thermochemically, guanylamintetrazole is strictly a "coolant" since it lacks 57% oxygen and requires a large amount of energy for complete combustion to CO and H₂O. However, it does possess a large potential gas volume (0.063 mole /gm) and burns in the open air when ignited with a match. Compositions cooler than M-15 can be formulated containing 15% guanylamintetrazole, possessing approximately 5% less ballistic potential. In view of its high nitrogen content and excellent physical and stability properties, this compound is certainly worthy of further consideration as a propellant ingredient.

23. Stollé also prepared the nitric acid salt of guanylamintetrazole by treating a dilute solution of hydrogen azide with dicyandiamide and nitric acid (Ref K).



This same salt was prepared at Picatinny by recrystallizing guanylamintetrazole out of hot 3M nitric acid. The salt crystallizes out in glistening platelets which decompose sharply at 183°C with a brilliant orange flash. Elemental analysis of a sample of this material, which had been dried to constant weight at 80°C, indicated that it possessed one-half a molecule of water of crystallization. This fact was not reported by Stollé. It was found that this half molecule of water can only be removed after heating the salt at 100°C for at least 24 hours. The resulting anhydrous form

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DISCUSSION OF RESULTS: (contd)

lost no weight when heated for an additional 72 hours at that temperature. When heated for 40 hours at 90°C under vacuum, a one-gram sample of the hemi-hydrate evolved 0.35 ml gas. Since the anhydrous form has a tendency to regain its half molecule of water, it was decided to test the nitric acid salt as the hemi-hydrate. The compound can be detonated at 10 inches with a 2 kgm weight and explodes at 180°C in the Explosion Temperature Test. It is approximately 2% soluble in water at 25°C and is non-hygroscopic. Although a saturated aqueous solution has a pH of 1.79 at room temperature there is no appreciable hydrolysis on further standing. The hemi-hydrated salt can also be considered thermally compatible with nitrocellulose. Guanylamminotetrazole nitrate possesses 56% nitrogen, lacks 16% oxygen for combustion to CO and H₂O, and, when ignited with a match, burns readily, leaving a small yellowish residue. It requires more energy for combustion than nitroguanidine and, therefore, should be a more effective coolant. In view of its many desirable characteristics, this compound is also worthy of further consideration as a possible addend for improving performance of propellant compositions.

24. Except for Stollé's original work in 1929, no other reference was found in the open literature concerning guanylamminotetrazole or its derivatives. It was, therefore, assumed that the dehydrated product of the nitric acid salt, namely, nitroguanylamminotetrazole had either never been previously prepared or, if so, never reported. The calculated thermochemical properties of this compound indicated that, based on its structure alone, it would offer all the advantages of a superior propellant ingredient since it incorporates the best features of both nitroguanidine and tetrazole. Because it contains two phosphoric groups and also possesses a slight positive energy required for combustion, it should be easily ignitable and also burn readily. Since it contains a high percentage of nitrogen (65%) and is not too poorly oxygen-balanced (-18.6%), it should impart low flash and smoke characteristics to propellant compositions. Based on the observed physical and chemical properties of guanylamminotetrazole and its nitric acid salt, it was believed that the corresponding nitramine would also possess desirable characteristics.

25. The most logical synthesis of nitroguanylamminotetrazole would naturally be from the dehydration of the nitric acid salt of guanylamminotetrazole. However, all ordinary dehydration mediums used failed to yield the desired nitramine (See Table V). Concentrated sulfuric acid evidently decomposes the entire molecule, as no product was obtained after quenching on ice; the use of acetic anhydride as a dehydration medium resulted in a recovery of the original nitric acid salt. When guanylamminotetrazole was used as the starting material, none of the ordinary nitration mediums gave the desired nitro compound. Finally, when the parent amine was added

DISCUSSION OF RESULTS: (contd)

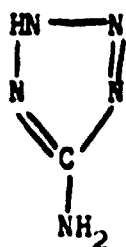
to a mixture of anhydrous phosphorous pentoxide dissolved in 100% nitric acid, quenching on ice resulted in formation of essentially guanylaminotetrazole nitrate plus a very small quantity (ca 3%) of nitroguanylaminotetrazole. Only such extreme nitration conditions yielded the desired product and always in the same small percentage yield. The nitramino derivative was separated from the nitric acid salt by washing the latter out with hot water, the former being very highly insoluble. Because of the extreme difficulty involved in its preparation by this method, only enough sample was prepared sufficient for the determination of a few important properties.

26. As mentioned above, nitroguanylaminotetrazole turned out to be surprisingly insoluble in water (0.02% at 25° and 0.04% at 60°C). Since it was even more insoluble in the common organic solvents, the sample was recrystallized from a large volume of hot water. Although elemental analysis (Table I) indicated that the material was essentially the desired compound, it is believed that the sample was not entirely free of impurities. When heated at 100°C for 96 hours, the sample lost 0.70% of its weight and at 30°C and 90% RH, it was 3% hygroscopic. A purer material would probably be more favorable in these two respects. The compound was also found to be quite compatible with nitrocellulose at 100°C. When heated on a hot stage melting point apparatus, the compound started to decompose at 247°C. When ignited in the open with a match, nitroguanylaminotetrazole burned (or decomposed) rapidly with little smoke and no residue. The physical and stability characteristics of this material therefore indicate that it is highly desirable as an addend to nitrocellulose propellants. Its chief advantage is that it can be substituted for nitroguanidine in the M-15 formula, along with triethylene glycol dinitrate (TEGN) instead of the more sensitive and less stable nitroglycerin, to yield a composition with essentially the same calculated internal ballistics as M-15 Propellant (See Table VII).

27. It is worthwhile, at this point, to consider some of the theoretical concepts concerning the structure and chemistry of the 5-aminotetrazoles which may throw some light on the difficulty involved in the nitration of guanylaminotetrazole. While doing this work it was recalled that, two years previously, similar results were obtained when it was attempted to prepare nitroaminotetrazole from either 5-aminotetrazole or its nitric acid salt. When the salt was treated with concentrated H_2SO_4 , decomposition resulted. When the same compound was treated with acetic anhydride, the original salt was recovered. Similarly, when 5-aminotetrazole, itself, was treated with mixed acid, decomposition occurred, and when treated with concentrated nitric and acetic anhydride, the nitric acid salt was recovered. Herbst, Roberts and Harvill (Ref L) suggest that in 5-aminotetrazole, the

DISCUSSION OF RESULTS: (contd)

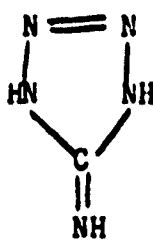
basic properties of the amino group are masked by the existence of the following tautomeric forms:



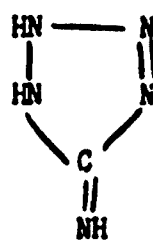
I



II

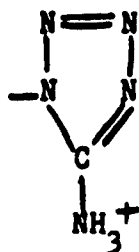


III

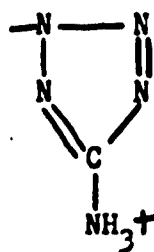


IV

In addition to the above structures it is also conceivable to postulate two additional forms of a zwitter-ion nature, i.e.

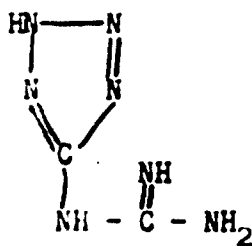


V

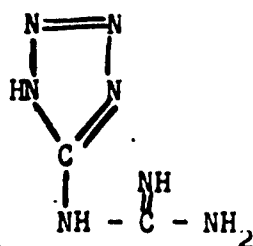


VI

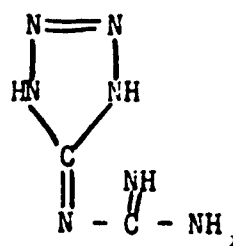
Whereas structures I - IV explain the acidity and metal salt formation of 5-aminotetrazole, structures V and VI more readily explain the high melting crystalline state of the compound as well as the formation of salts with mineral acids such as hydrochloric and nitric. Analogously, similar structures can be drawn for guanylaminotetrazole.



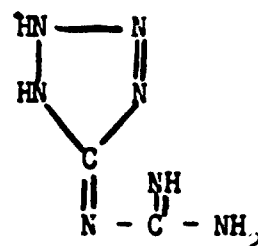
VII



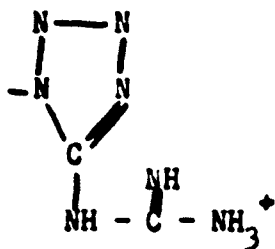
VIII



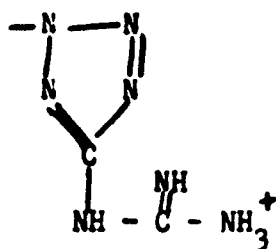
IX



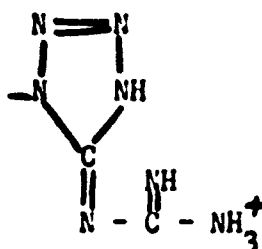
X

DISCUSSION OF RESULTS: (contd)

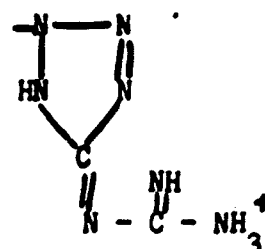
XI



XII



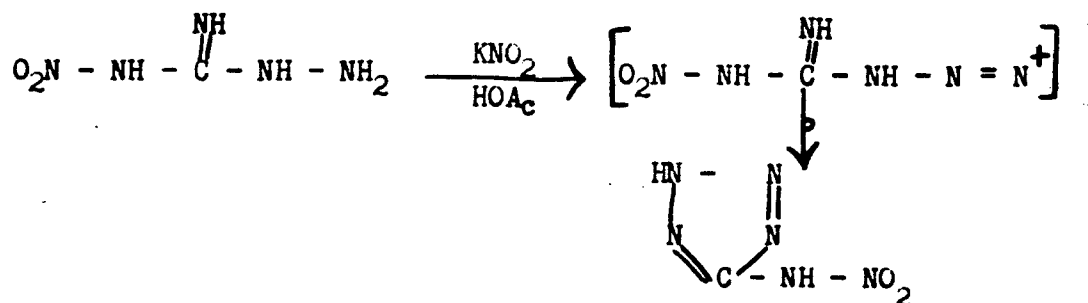
XIII



XIV

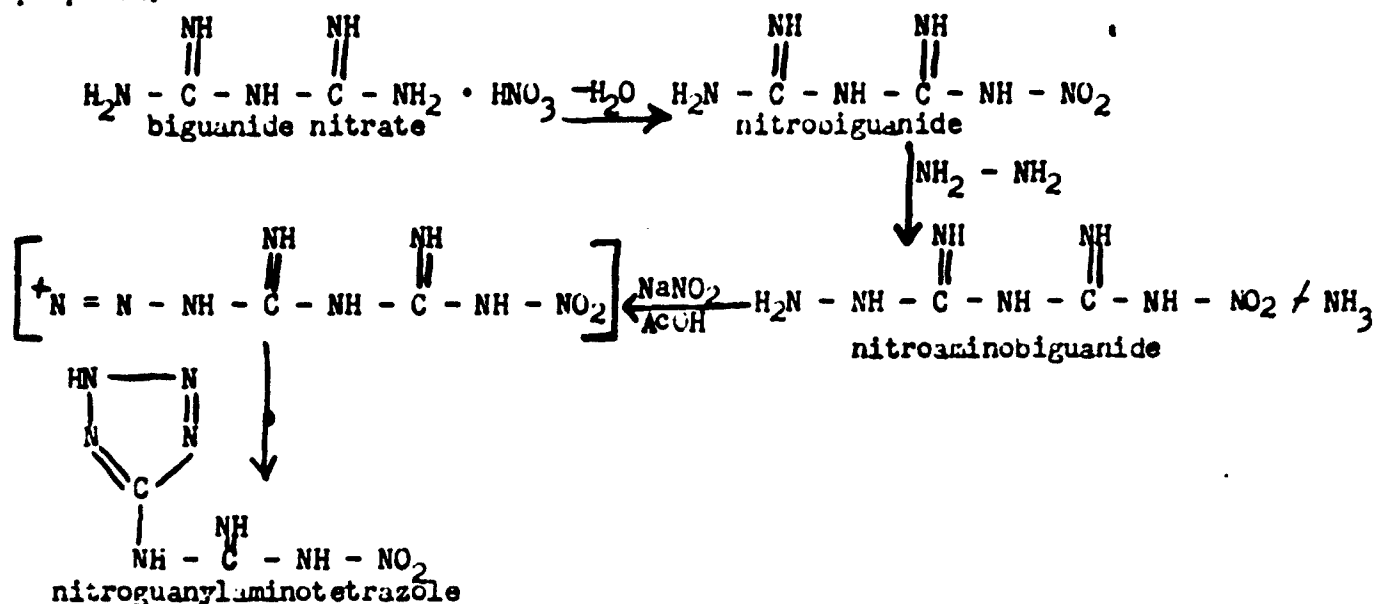
It can be seen that four zwitter-ion structures are possible for guanylamino-tetrazole and it is believed that this internal ionic character plays an even more important role in accounting for the properties of this compound than it does for the analogous aminotetrazole. This is indicated by the fact that guanylamino-tetrazole does not melt at 300°C, is only slightly acidic in aqueous solution and forms a salt readily with nitric acid. In addition, the resulting nitric acid salt can be hydrolyzed back to yield the parent compound only after long boiling in aqueous solution, indicating that the ammonium nitrate type of linkage formed is also quite strongly ionic in character. In view of these considerations, it can be postulated that in a strong nitric acid medium, the tendency for guanylamino-tetrazole to undergo salt formation and retain this structure will be much greater than the tendency to dehydrate to the covalent nitramine, the formation of which undoubtedly requires a great deal more energy. It is true that under such extreme nitration conditions as with 100% nitric acid and phosphorous pentoxide, some nitroguanylamino-tetrazole will form but only in yields so insignificant as to be considered as an impurity. That these small amounts of nitro compound can be isolated at all is attributed to the high insolubility and stability of the substance once it is formed.

28. Lieber, et al, (Ref M) have since been able to prepare nitroamino-tetrazole but by an indirect method, i.e., the reaction of nitrous acid with nitroaminoguanidine. This involves a diazotization of the hydrazine amino group followed by a cyclization to form the tetrazole ring. The reaction can be represented as:



DISCUSSION OF RESULTS: (contd)

Since it is not feasible to prepare nitroguanylamintetrazole by a direct nitration of guanylamintetrazole, it would be desirable to investigate some such indirect method of synthesis in which the nitramine group is already present in one of the starting materials. The most logical method that naturally suggests itself involves the diazotization of nitroaminobiguanide. Since nitroaminoguanidine is prepared by the reaction between hydrazine and nitroguanidine, the following synthesis for nitroguanylamintetrazole is proposed:



Neither nitroaminobiguanide nor nitrobiguanide have previously been described in the literature and it is planned to study this series of reactions in the Picatinny research laboratories.

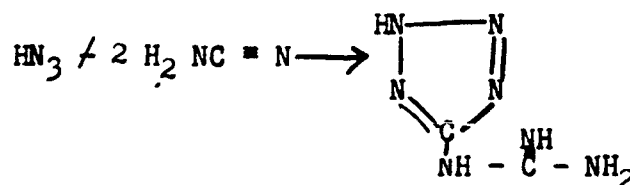
29. Utilizing those compounds which have been evaluated as possessing adequate physical properties for inclusion in nitrocellulose propellants, compositions have been formulated to illustrate their ballistic possibilities and these are presented in Table VII. These compositions are compared with M-15 Propellant using the Herschfelder calculations (Ref N) for "relative force", gas volume, flame temperature, heat of explosion and oxygen balance. Each composition represents that formulation containing a particular high nitrogen compound which was calculated to give the highest "force" at a flame temperature equal to that of M-15 Propellant. Urazine, N-guanyloxamic acid, nitrobiuret and cyamelide yield cool compositions with approximately 10% less "force" than M-15 Powder but with better oxygen balances. Guanylamintetrazole and its nitric acid salt can be incorporated in cool powders with 5% less "force" and nitroguanylamintetrazole with equal or slightly higher "force"

DISCUSSION OF RESULTS: (contd)

than M-15 and all with about the same oxygen balance. On an overall basis, nitrobiuret and the three tetrazole derivatives are superior propellant ingredients to the other three compounds; because of their phosphoric nature they should yield cool powders with more satisfactory "quickness" rates.

30. In formulating the hypothetical compositions in Table VII, triethylene glycol dinitrate (TEGN) was used as the plasticizer instead of nitroglycerin. It was found that where high nitrogen compounds are included in cool compositions with nitrocellulose, the use of NG, instead of TEGN, does not offer any particular advantage as far as calculated "force" is concerned since with the former material, higher temperatures are obtained at the expense of gas volume; the use of TEGN, however, results in higher gas volumes at the desirable lower temperatures. In addition, TEGN is more stable, less volatile, much less sensitive and possesses colloidizing action equal to NG (Ref O). In view of these considerations and also because NG is particularly undesirable because of the explosive hazards involved in its industrial manufacture, it is felt that TEGN is a superior plasticizer for cool nitrocellulose propellants and especially for those containing high nitrogen compounds.

31. In evaluating materials as possible future propellant ingredients, a consideration of the availability of the substance is necessarily important. Urazine and N-guanyloxamic acid depend upon hydrazine as a starting material. Although these compounds, by virtue of their excellent stability and physical properties, offer possibilities of being good cool propellant ingredients, they cannot be considered beyond the laboratory stage at this time since hydrazine is not now commercially available in large quantities. A program to study the basic chemistry of hydrazine synthesis was forwarded to the Office, Chief of Ordnance (ORDTB), Ref P. As yet, no action has been taken on this program. Cyamelide, although possessing excellent coolant properties along with a good oxygen balance, depends upon free cyanic acid for its preparation. Its manufacture from available materials, in good yields, is also not considered feasible at the present time. Nitrobiuret, however, depends on urea and can be made readily available if so desired. If this material will yield physically and thermally stable finished propellants, it should offer a good economical source of cool powders. No accurate prediction as to the availability of guanylaminotetrazole can be made at this time. However, it is possible that this material can be produced by the condensation of hydrogen azide (derived from sodium azide) with two moles of cyanamide.



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EXPERIMENTAL PROCEDURE:

32. Samples of urazine, carbonylhydrazide oxalate and N-guanyloxamic acid were received from the University of Illinois and evaluated as such. For detailed descriptions of the preparation of these compounds see Ref A.

33. Preparation of Nitrobiuret

100 gms of anhydrous biuret were slowly added to an ice cold mixture of 66 ml nitric acid (70%) and 250 ml concentrated sulfuric acid with constant stirring. The addition of the solid was so controlled as to keep the reaction mixture at 0°C. After all the biuret was added, the mixture was stirred for an additional two hours, keeping the temperature at 0°, until all solid substance dissolved. The entire mixture was then poured on cracked ice and the white powdery nitrobiuret which formed was filtered and washed with water and alcohol. Upon recrystallization from warm water, a 75% yield of pure nitrobiuret is obtained, MP 170°C with decomposition.

34. Preparation of Dinitrobiuret

27.6 gms of nitrobiuret were dissolved in 50 gms of 100% nitric acid cooled to 5°C. The solution was then placed in a vacuum desiccator over soda lime and concentrated sulfuric acid (separated from each other) and concentrated in the dark until a white crystalline material formed. The dinitrobiuret, still wet with residual nitric acid, was then spread out on a porous clay plate and dried in air for 2 hours. The material was then dissolved in a minimum amount of warm absolute methanol and precipitated out by chilling. The white needle-like crystalline dinitrobiuret was filtered, washed with ether and air dried. MP 124°C (Verpuffen).

35. Preparation of Diaminobiuret

For a detailed preparation of this compound see Ref D.

36. Preparation of Cyamelide

100 gms of oxalic acid dihydrate and 100 gms of potassium cyanate (C.P.) were ground together in a large mortar for one hour. The solid mixture first becomes wet and pulpy and then solidifies again into a dry powdery mass. The mixture was then allowed to digest at ordinary temperatures in the hood until the odor of cyanic acid was no longer intense. The residue was then taken up with 200 ml of hot water and stirred in a beaker for one hour. Separation of the cyamelide from the wash water was best accomplished by centrifugation. The water-washing procedure was repeated three times. The material was then washed twice with acetone, filtered, air-dried and then placed in an oven at 80°C overnight. Yield, 12 grams.

EXPERIMENTAL PROCEDURE: (contd)37. Preparation of Hydrazonium Oxalate

58.8 gms of 85% hydrazine hydrate were added slowly with stirring through a dropping funnel to a hot solution of 126 gms of oxalic acid dihydrate in 150 ml of water. A white precipitate began to form after about one-fourth the addition of the hydrazine. After all the hydrazine was added, the mixture was stirred for one hour at 90°C and then allowed to cool to room temperature. The precipitate was filtered through a Büchner funnel, washed with cold water, alcohol and ether, and dried in air. The crude yield of hydrazonium oxalate, weighing 112 gms, was purified by recrystallization from hot water. MP 181°C, dec.

38. Preparation of Hydrazonium Nitrate

One (1) mole of hydrazine hydrate (59 gms of 85% solution) was mixed with 30 ml water in a beaker equipped with a mechanical stirrer and cooled in an ice bath. 65 ml of 70% nitric acid, diluted to 100 ml with distilled water, were added slowly from a dropping funnel keeping the temperature between 10 - 15°C. When the addition of the acid was complete, the solution was stirred for an additional hour allowing it to warm up to room temperature. The solution was then concentrated on the steam bath to a volume of 25 ml. Upon the addition of 75 ml of 95% ethanol to the cooled concentrate, a white precipitate of hydrazonium nitrate formed. This was filtered, washed with alcohol and ether, and dried in an oven at 50°C to constant weight. Yield 50 grams, MP 70 - 71°C.

39. Preparation of Cyanamid Solutions - (from "Inorganic Synthesis", Vol III)

Aqueous Solution - 300 gms of crude calcium cyanamide (approx 60%) was made into a slurry with 300 ml of water. The slurry was then placed in a 7" Büchner funnel connected to a long efficient reflux condenser which was in turn connected to a 4-l filter flask immersed in an ice bath. 1800 ml of water, warmed to 70°C, was then poured onto the slurry in the Büchner funnel at such a rate as to leave a thin layer of water above the slurry at all times. This was accomplished by applying a very slight suction through the filter flask by means of a vacuum line. The resulting solution (in the filter flask) of calcium hydrogen cyanamide was then treated with 20% sulfuric acid until the pH reached a value of 5. This required approximately one liter of sulfuric acid solution. The calcium sulfate (172 gms) thus precipitated was removed by filtration. The resulting cyanamide solution was concentrated down to 300 ml by means of a water aspirator (10 - 12 mm mercury pressure) using a 10" fractionating column (to prevent mechanical loss of the cyanamide which has a tendency to distill over with the water). Based on the amount of calcium sulfate precipitated, it is estimated that

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EXPERIMENTAL PROCEDURE: (contd)

approximately 1 mole (42 grams) of cyanamide in aqueous solution can be produced in this manner.

Alcoholic Solution - 300 gms of crude calcium cyanamide were placed in a 3-liter beaker with 700 ml of 95% alcohol. The beaker was surrounded by an ice bath and the mixture was made into a slurry using a very efficient heavy-duty mechanical or air-driven stirrer. A solution consisting of 450 ml of 50% sulfuric acid diluted with 100 ml of water was added slowly through a dropping funnel with continued vigorous stirring. As more and more calcium sulfate was formed, the mixture became thicker and more difficult to stir. When 500 ml of the sulfuric acid solution had been added, the pH of the mixture was checked and additional acid was added carefully until the pH was 5. The mixture was then filtered through a large Büchner funnel and the filter cake extracted with three 200-ml portions of hot 95% ethanol. The filtrate was then concentrated on the steam bath to one-half its original volume and a small amount of additional calcium sulfate, which had precipitated, was filtered off. The yields of cyanamide obtained in this manner were approximately the same as from the water-extraction method.

40. Preparation of Guanylamintetrazole

The cyanamide solution (prepared from either method in Section 39) was neutralized to a pH of 7 with dilute ammonium hydroxide. One mole of 5-aminotetrazole was added and the mixture was immersed in a steam bath and heated with stirring for a period of five hours. The 5-aminotetrazole went into solution after 30 minutes and upon continued heating and concentration of the mixture, guanylamintetrazole began to precipitate. After the five-hour heating period, the crude product was filtered from the hot mixture. The yield of product was improved by dilution of the mother liquor (which precipitated some 5-aminotetrazole on cooling) with water and further concentration on the steam bath. The best yield of crude material, obtained in this manner, was 70 grams or 55% of theory. Ten (10) grams of crude guanylamintetrazole were recrystallized from 800 ml of hot water (85°C). The pure material did not melt at 300°C.

41. Preparation of Guanylamintetrazole Nitrate

Ten grams of pure guanylamintetrazole were dissolved, with stirring, in 150 ml of hot 3M nitric acid solution. The hot solution was filtered and, upon cooling, shiny white platelets of the nitric acid salt crystallized out. These were filtered, washed with cold water, alcohol and ether, and then dried in an oven at 80°C. The compound decomposes sharply with an orange flash at 183°C.

EXPERIMENTAL PROCEDURE: (contd)43. Preparation of Nitroguanylamintetrazole

Ten grams of guanylamintetrazole were slowly added to 50 ml 100% nitric acid with constant stirring, keeping the temperature at -10°C . When all solid material had dissolved, 6 grams of anhydrous P_2O_5 were added slowly at the same temperature. Stirring was continued for an additional hour and then the entire mixture was slowly poured onto 300 grams of cracked ice with continued rapid stirring by hand. A fine, white precipitate formed immediately. This was filtered on a Büchner funnel and the resulting solid which consisted essentially of guanylamintetrazole nitrate was washed with several 100-ml portions of hot water until only a very small amount of brown insoluble material (0.3 gram) remained on the filter. This small amount of crude nitroguanylamintetrazole was dissolved in 300 ml of very hot water and recrystallized by chilling to 0°C . The dried product began to decompose at 247°C on a hot stage melting apparatus.

All laboratory tests were made in accordance with procedures standard at Picatinny Arsenal.

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- O. Picatinny Arsenal Technical Report No. 1638
- P. Letter from Picatinny to Chief of Ordnance, ORDBB 471.86/55,
dated 6 October 1950

INCLOSURES:

Tables I - VII
Figure I

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TABLE I

COMPOSITION CHARACTERISTICS OF HIGH NITROGEN COMPOUNDS

Compound	Empirical Formula	Mol. Wgt.	C/H	% Oxygen Balance ^a	Elemental analysis			Additional Analytical Data (Found)
					Calc	Found		
					C	H	N	
Urazine	$C_2H_4N_3O_2$	116	0.50	-28	20.7	3.44	48.3	e
Carbohydrazide oxalate	$C_3H_7N_4O_5$	180	0.38	-18	20.0	4.44	31.1	e
N-guanyloxamic acid	$C_3H_5N_3O_3$	146	0.60	-33	24.7	4.12	38.4	e
Nitrocinurel	$C_2H_4N_3O_4$	148	0.50	0	16.2	2.70	37.9	37.9 ^c
Dinitrocinurel	$C_2H_3N_5O_6$	193	0.66	+21	12.4	1.55	36.3	36.4 ^c
Diaminocinurel	$C_2H_7N_5O_2$	133	0.29	-42	18.1	5.26	52.6	52.4 ^c
Cyamelide	$(CHNO)_x$	(43)x	1.00	-19	27.9	2.33	32.6	32.5 ^d
Hydrazine oxalate	$C_2H_6N_2O_4$	122	0.33	-13	19.7	4.92	22.9	%C, 26.4; %H, 3.45
Hydrazine nitrate	$H_5N_3O_3$	95	—	+8 ^b	—	5.26	44.2	% Oxalic acid, 73.8 Theor. 73.7
Guanylaminetetrazole	$C_2H_5N_7$	127	0.40	-57	18.9	3.94	77.2	%HNO ₃ , 64.7 Theor. 66.3
Guanylaminetetrazole nitrate (hemi-hydrate)	$C_2H_6N_8O_3 \cdot \frac{1}{2}H_2O$	199	0.29	-16	12.1	3.52	56.3	%C, 12.21; %H, 2.96 Loses 4.75% H ₂ O at 100°C, Theor. 4.53%
Nitroguanylaminetetrazole	$C_2H_4N_8O_3$	172	0.50	-19	14.0	2.32	65.1	%C, 13.8; %H, 2.72

^a To CO & H₂O^b To N₂ & H₂O^c Combustion method^d Kjeldahl method^e Tested as received from Univ of Illinois

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TABLE II
PHYSICAL AND EXPLOSIVE PROPERTIES OF HIGH NITROGEN COMPOUNDS

Compound	M.P. °C	Density gms/cc	% Hygros. (30°C-90% RH)	Impact Test 2kgm. wt inches	Exp. Temp Test °C
Urazine	275-6 dec.	1.62	nil	—	—
Carbohydrazide oxalate	173 dec.	1.70	nil	—	—
N-guanyloxamic acid	210	1.71	nil	—	—
Nitrobiuret	170 dec.	1.71	nil	30	190 (smoke)
Dinitrobiuret	124 dec.	—	3	6	165
Diaminobiuret	200-1	1.57	nil	—	—
Cyamelide	>300	—	5	—	—
Hydrazine oxalate	181 dec.	1.70	nil	—	—
Hydrazine nitrate	70 - 71	—	deliq.	13	225
Guanylaminetetrazole	>300	1.48	nil	40 ^a	265 (smoke)
Guanylaminetetrazole nitrate (heml-hydrate)	183 dec.	1.58	nil	10	180
Nitroguanylaminetetrazole	247 dec.	—	3	—	—

^a Weight of charge used.

TABLE III

CHEMICAL PROPERTIES OF HIGH NITROGEN COMPOUNDS

Compound	pH of a Sat. Aqueous ¹ Sol. after			Solubility, gms per 100 ml. Solvent			
	1 hour at 25°C	2 hours at 60°C	24 hours at 60°C	water 60°C	95% alc 25°C	acetone 25°C	
Urazine	3.52	3.31	3.55	1.09	3.20	0.03	0.02
Cyrocyanhydrazide oxalate	3.01	3.05	3.04	0.22	1.51	0.01	0.07
N-guanidoxamic acid	4.35	4.35	4.40	0.05	0.23	nil	nil
Nitroisouret	1.84	1.90	6.89	0.68	2.75	0.24	0.73
Dinitroisouret	dec.	—	—	dec	dec	10.4	24.7
Diaminooisouret	6.88	6.95	6.59	18.2	v.s.	0.11	0.14
Cyanamide	6.85	6.63	6.29	0.03	0.07	nil	0.02
Hydrazine oxalate	2.09	2.63	2.68	1.70	5.28	0.01	0.08
Hydrazine nitrate	4.00	3.96	—	v.s.	v.s.	—	—
7-aminotetrazole	5.31	5.40	5.42	0.35	0.91	0.03	0.02
Guanylaminotetrazole nitrate (hemihydrate)	1.79	1.70	1.70	1.92	2.76	0.62	0.05
Nitroguanylamino-tetrazole	—	—	—	0.02	0.04	—	—

¹ g of distilled water and 5.60

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TABLE IV

THERMAL STABILITY CHARACTERISTICS OF HIGH NITROGEN COMPOUNDS

Compound	Heat Test			Vac. Stab. Test			Heat Test in films ^a with EC		
	Loss in wt, %			°C ml. gms hrs			(13.15%N), 75/25 Comp		
	°C	1st 48 hrs	2nd 48 hrs	°C	ml. gms	hrs	°C	1st 48 hrs	2nd 48 hrs
Urazine	100	0.00	0.06	120	0.35	1	100	3.39	0.08
Carbohydrazine oxalate	100	3.30	1.40	120	117	1	100	5.51	0.82
N-methyloxamic acid	100	0.00	0.05	120	0.34	1	100	2.93	0.40
Nitrosouret	100	16.78	13.76	-	-	-	100	9.83	4.41
	75	0.19	0.32	-	-	-	75	2.47	0.80
Dinitrotriazolene	75	71.36	20.57	-	-	-	-	-	-
Dinitrotriazolene	100	3.28	1.67	-	-	-	100	13.6	3.58
Cyamelide	100	0.44	0.15	90	1.86	1	100	3.87	0.50
Hydrazine oxalate	100	0.33	0.17	120	4.19	5	100	10.25	3.44
Hydrazine nitrate	100	nil	nil	120	0.02	5	75	3.19	0.90
Guanylamino-tetrazole	100	0.73	0.05	120	0.41	1	75	19.26	1.31
Guanylamino-tetrazole nitrate (hemihydrate)	100	4.75	nil	90	0.35	1	100	4.57	0.57
Nitroguanylamino-tetrazole	100	0.52	0.20	-	-	-	100	5.83	0.55
Nitrocellulose film (13.15%N)	-	-	-	-	-	-	100	3.97	0.62
Nitroguanidine	100	0.013	0.09	120	0.44	5	100	4.00	0.07
							75	2.76	0.30
							100	1.58	0.00

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^a All films prepared using methyl ethyl ketone as solvent^b Losses up to 4% during the first 48 hrs can be attributed to solvent

TABLE V

ATTEMPTED PREPARATIONS OF NITROGUANYLAMINOTETRAZOLE

Starting Material	Nitration or Denaturation Medium	Temp (°C)	Product obtained after quenching on ice
Guanylamminotetrazole nitrate	conc. H_2SO_4	0	none (decomposition occurred)
"	acetic anhydride	0	Guanylamminotetrazole nitrate
"	100% HNO_3 and conc H_2SO_4	0	none (decomposition occurred)
"	100% HNO_3 and acetic anhydride	0	Guanylamminotetrazole nitrate
"	100% HNO_3 and P_2O_5	0	Guanylamminotetrazole nitrate
Guanylamminotetrazole	70% HNO_3 and conc. H_2SO_4	-10	none (decomposition occurred)
"	100% HNO_3 and conc. H_2SO_4	-20	none (decomposition occurred)
"	100% HNO_3 and acetic anhydride	-10	Guanylamminotetrazole nitrate
"	100% HNO_3	-10	Guanylamminotetrazole nitrate
"	100% HNO_3 and P_2O_5	-10	Mixture containing nitroguanylamino-tetrazole in approx. 3% yield and Guanylamminotetrazole nitrate
"	100% HNO_3 and P_2O_5	30	none (decomposition occurred)

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TABLE VI
THERMOCHEMICAL PROPERTIES OF HIGH NITROGEN COMPOUNDS

Compound	$\frac{-\Delta E}{\text{found}}$	$\frac{\text{calc}}{Q}$	$\frac{n}{E}$	$\frac{Cv}{E/Cv}$		
Urazine	267.3	270	0.0517	-704	0.344	-2020
Carbohydrazide oxalate	316.1	316	0.0500	-947	0.391	-2420
N-Guanyloxamic acid	339.7	338	0.0547	-1165	0.367	-3180
Nitrobiuret	229.4	228	0.0406	-107	0.342	-314
Dinitrobiuret	206.1	203	0.0311	-506	0.316	-1600
Diaminobiuret	344.5	334	0.0602	-986	0.400	-2460
Cyanellide	1640 ^a	-	0.0465	-1328	0.313	-4240
Hydrazine oxalate	190.0	208	0.0492	-1000	0.413	-2420
Hydrazine nitrate	113.2	123	0.0422	-509	0.443	-1147
Guanylamino-tetrazole	406 (400) ^b	408	0.0630	-888	0.339	-2620
Guanylamino-tetrazole nitrate (hemi-hydrate)	363.5	365	0.0477	-274	0.358	-765
Nitroguanylamino-tetrazole	-	385	0.0465	-54	0.312	-172
Nitroguanidine	211	210	0.0481	-49	0.371	-132

$-\Delta E$ = Heat of Combustion, k cal/mole
 Q = Heat of Explosion, cal/gm
 n = Gas Volume, moles/gm
 E = Relative Energy in Gas Formed upon Combustion, cal/gm
 Cv = Mean Heat Capacity, cal/degree

^a cal/gm
^b value obtained at Purdue University

TABLE VII

CALCULATED INTERNAL BALLISTIC PROPERTIES OF COMPOSITIONS CONTAINING HIGH NITROGEN COMPOUNDS

Compound	Composition, %	n	Tv	"F"	Q	O.B.
Nitroguanidine	NC 20, NG 19, Nitroguanidine 55, EC 6	0.0464	2624	242	787	-12
Urazine.	NC 69, TEEN 10, Urazine 20, EC 1	0.0437	2547	221	751	-6
N-guanyloxamic acid	NC 74, TEEN 10, N-guanyloxamic acid 15, EC 1	0.0436	2518	218	740	-7
Nitrobiuret	NC 39, TEEN 15, Nitrobiuret 45, EC 1	0.0427	2540	216	764	-4
Cyamelide	NC 74, TEEN 15, Cyamelide 10, EC 1	0.0428	2546	217	-	-5
Guanylaminetetrazole	NC 69, TEEN 15, Guanylaminetetrazole 15, EC 1	0.0456	2534	230	744	-12
Guanylaminetetrazole nitrate (hemi-hydrate)	NC 51, TEEN 20, Guanylaminetetrazole nitrate (hemi-hydrate) 28, EC 1	0.0451	2543	228	765	-10
Nitroguanylaminetetrazole	NC 25, TEEN 19, Nitroguanylamino-tetrazole 55, EC 1	0.0467	2640	245	943	-15

N - Gas Volume, moles/gm
 Tv - Adiabatic Flame Temp, °K
 "F" - Relative Force, mole cal/mole (nRTv)

Q - Heat of Explosion, cal/gm
 O.B. - Oxygen Balance to CO / H₂O, %

NC - nitrocellulose (13.15%)
 NG - nitroglycerin
 TEEN - triethylene glycol dinitrate
 EC - ethyl centralite

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Figure 1

